

Diode-laser-based measurements of hydrogen fluoride gas during chemical suppression of fires

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Abstract. Near-infrared tunable diode laser (NIR-TDL) spectroscopy is used to quantify HF gas produced during fire suppressant testing of Halon alternatives. Results of comparisons with other techniques for measuring HF gas concentrations are discussed. Measurements of HF gas produced in laboratory and real-scale fire suppression testing are presented. The necessity for time-resolved measurements during testing of suppression systems designed to scavenge HF gas is demonstrated.

Fire and explosion suppression is of critical importance on board land combat vehicles. Currently, Halon 1301 (CF₃Br) is employed to suppress fires and explosions in most military vehicles. However, due to its high ozone depletion potential (ODP), Halon 1301 was banned from production by international agreement [1] as of 1 January 1994. A current, service-wide program [2] is underway to identify near-term, environmentally acceptable Halon alternative technologies.

Important properties for successful Halon alternatives are high suppression efficiency, low ODP, low suppressant residue after use, low electrical conductivity, stability under long-term storage, and non-toxicity prior to and during dispersion. Recent work [3] has shown that hydrogen fluoride gas (HF) is the principal toxic gas produced during fire suppression by Halon 1301 and by fluorocarbon-based fire suppressants. Therefore, for fluorocarbon-based Halon alternatives, minimization of HF gas production during fire suppression is an important criterion. The work presented here describes our efforts in using near-infrared tunable diode lasers (NIR-TDL) to measure HF gas produced during fluorocarbon-based chemical suppression of laboratory and real-scale fires.

1 Background

When a projectile penetrates the hull and fuel cell of a land combat vehicle, fuel cell penetration may result in a fine mist of fuel being dispersed into the crew compartment. The

ensuing “mist fireball explosion” [4] is extinguished within 250 ms of detection by the currently deployed Halon 1301 suppression system. Diagnostic equipment designed to measure HF gas produced during testing of Halon alternative systems needs to provide data on a time scale shorter than the suppression event. The extreme reactivity of HF gas dictates the additional requirement that the measurement be made in situ.

NIR-TDL absorption spectroscopy for HF measurement provides the mid-range sensitivity (50–5000 ppm) [2], speed of data collection, and ability to use low-replacement-cost optics and detectors necessary for data sampling in hostile environments. These commercially available diode lasers, initially produced for optical communication, began to see use for measurement of HF gas in the early 1980s [5]. Today, relatively low cost narrow-band diode lasers emitting near-infrared radiation at wavelengths absorbed by HF gas ($\sim 1.3 \mu\text{m}$ wavelength-overtone transition) are commercially available. Use of NIR-TDLs for measuring HF gas is now an accepted method for industrial applications [6, 7]. Diode lasers emitting in the mid-infrared region at wavelengths where HF absorbs (2.5 μm wavelength-fundamental transition) are not yet commercially available.

2 Experimental

The experimental apparatus does not appreciably change according to the type of fire being investigated. Figure 1 shows a schematic of the experimental setup and signal processing electronics. For experiments described here, an InGaAsP distributed feedback (DFB) near-infrared tunable diode laser (Sensors Unlimited, Inc.) operating near 7665 cm^{-1} (corresponding to P(2) of the first vibrational overtone of HF [8]) is mounted in a temperature-controlled laser diode mount (ILX Lightwave model LDM-4980). The temperature of the diode mount is controlled by a thermoelectric temperature controller (ILX Lightwave model LDT-5412). Laser diode current and internal TEC control are provided by a laser diode controller (ILX Lightwave model 3700). A low-frequency sawtooth modulation ($\sim 100 \text{ Hz}$, Tektronix FG 504 function

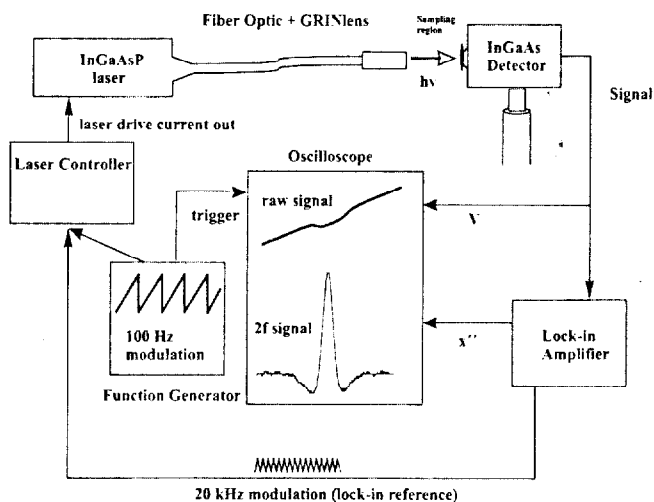


Fig. 1. A schematic of the experimental apparatus and signal processing electronics used in these experiments. V is the signal prior to demodulation; x'' is the signal following demodulation at twice the reference frequency

generator) is combined with a higher frequency modulation (~ 20 KHz, sine output from a SRS model 830 DSP lock-in amplifier). This modulation is superimposed onto the laser drive current, allowing the laser wavelength to be scanned through the spectral region of interest (low-frequency modulation) while also providing a high-frequency wavelength "dither" to allow second-harmonic signal detection.

The wavelength modulated radiation from the laser diode is fiber coupled. This fiber is terminated by a gradient index (GRIN) lens (Sentech Systems, Inc.), which collimates the laser radiation (beam diameter approximately $400\ \mu\text{m}$). The GRIN lens-tipped fiber is placed into a small test rig designed to maintain fiber and detector alignment. Laser radiation is detected by using an InGaAs detector [active area $2\text{ mm} \times 2\text{ mm}$ (Epitaxx)]. The path length from the GRIN lens to the detector is typically 10 cm. The modulated detector signal is demodulated at twice the higher frequency modulation (SRS model 830 DSP lock-in amplifier, typically operated with a time constant of $100\ \mu\text{s}$), the second-derivative line-shape displayed on an oscilloscope (LeCroy model 9354), and the output from the oscilloscope transferred to and stored on a laptop computer. The DC output level of the detector is continuously monitored by the LeCroy oscilloscope (bandwidth 500 MHz).

3 Measurements in particle laden environments

Normal fixed wavelength transmission spectroscopy cannot distinguish between light attenuation (measured at the detector) resulting from gas absorption or light scattering such as might occur in a smoke- or soot-filled environment. Partly for this reason, we employ derivative spectroscopy to enable us to account for contributions to light attenuation by scattering from particulate matter. In this method, the laser output wavelength is scanned through a wavelength range that includes the wavelength of absorption of the gas species of interest (HF). A lock-in amplifier is used to measure the change in detector signal intensity with the change in wavelength. Attenuation of laser radiation by a ro-vibrational transition of a small

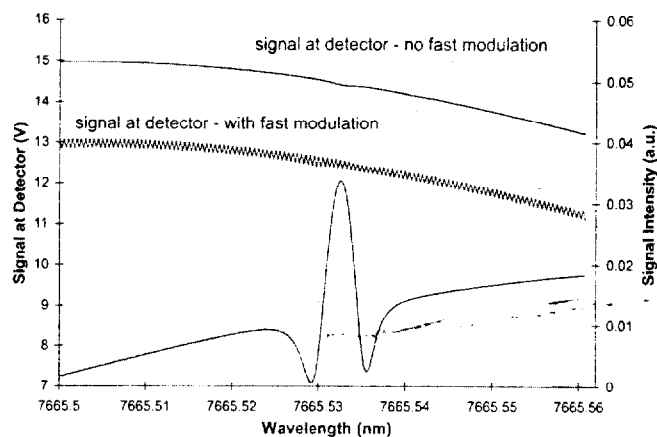


Fig. 2. A graphical simulation of signal processing for $2f$ measurement of HF gas concentrations. The slope in the baseline is caused by the change in laser diode output power with laser drive current

gas molecule is detected because the wavelength range of the scan is several times the width of the spectral absorption feature (typically on the order of 0.1 cm^{-1} at atmospheric pressure). Because light scattering by particulate matter is nearly constant over the very small wavelength range of the laser scan, the change in detector signal intensity with the change in wavelength is effectively zero in the absence of any absorbing gas. However, because the derivative signal is also proportional to the background signal intensity, the second-derivative signal is divided by the DC signal to account for light scattering by particles.

Second-harmonic detection using tunable diode lasers has been extensively discussed in the literature [9]. Figure 2 shows a graphical simulation of the signal processing employed in these experiments. Briefly, the laser output wavelength is slowly scanned through a spectral region where HF gas absorbs (in this case, $P(2)$ of the first vibrational overtone). The output at the detector during the laser scan (with the high-frequency modulation turned off) may be seen in the upper trace of Fig. 2. A small-amplitude high-frequency modulation is superimposed on the laser drive current (middle trace in Fig. 2). Demodulation at twice the frequency of the small-amplitude high-frequency laser drive modulation yields the second-derivative signal shown in the lower trace in Fig. 2. It should be noted that the upper trace in Fig. 2 shows that the laser diode output power has a non-linear dependence on the laser drive current. While this is non-ideal behavior, in our experience this is a common trait of commercially available laser diodes. The non-linear power output dependence on laser drive current (exaggerated here for illustration) causes the sloping baseline for the second-derivative signal in Fig. 2. For measurements at extremely low concentrations or for gases with small absorption cross sections, the non-linearity of laser diode output power with laser drive current may affect limits of detection.

4 Calibration

Calculation of HF gas partial pressure relies upon the Bouguer-Lambert Law [10], which states that for optically thin media at the absorption line center, the negative loga-

rithm of the fraction of transmitted light intensity (referred to as absorbance, A) is equal to the absorption coefficient of the molecule of interest (α) times path length (L) times pressure (P): $A = \alpha LP$. Since the absorption coefficient, α , is constant, and L is known, a measurement of absorbance, A , is sufficient to determine pressure, P . The second-derivative signal peak height may be shown [8] to be proportional to A :

$$\ddot{X}/V = kA \quad (1)$$

Here, \ddot{X} is the peak height of the second-derivative signal (volts), V is the DC voltage measured by the detector in the absence of any molecular absorbance, and k is a constant which includes the measuring instrument and optics function. Letting S , the $2f$ signal peak height (peak-to-trough height, the distance between the maximum and minimum points on the $2f$ signal), equal \ddot{X}/V yields

$$S = (k\alpha)LP \quad (2)$$

The slope of a plot of LP versus S provides the value of $k\alpha$. A calibration of the system with known concentrations of the absorbing gas must be performed to determine the value of $k\alpha$. Once this value is known, the HF gas pressure (P) may be obtained directly from (2). Care must be exercised so that HF degradation of optical surfaces during measurement does not affect the value of $k\alpha$, since this value is instrument function dependent. For this reason, calibration should be performed at the beginning and end of each measurement set. Additionally, for HF concentrations which attenuate more than 5% of the incident light, the linear relationship between HF gas pressure and $2f$ signal peak height may no longer hold [11].

5 Comparison with other techniques

A flow cell was constructed to allow simultaneous measurement of HF gas mixtures (HF in N_2) using NIR-TDL absorption spectroscopy, Fourier transform infrared (FT-IR) spectroscopy, and a fluoride-ion selective electrode (ISE). The flow cell is designed with five radial sampling ports at four longitudinal distances from the gas inlet port. All measurements were made at atmospheric pressure. A schematic of the flow cell is shown in Fig. 3. Results from measurements of HF gas using the three techniques are shown in Fig. 4. The limit of detection (LOD) at atmospheric pressure of HF gas from the NIR-TDL absorption spectroscopy apparatus described here is approximately 40 ppm (corresponding to approximately 2×10^{-4} absorbance units). It may be possible to improve upon our current LOD by moving to higher modulation frequency, but at present we are limited by the $2f$ demodulation frequency (100 KHz) of our lock-in amplifier.

Calibration of the FT-IR data was done with the peak absorbance of the R(3) line of the fundamental ($\nu = 0 - 1$) vibrational transition. The limit of detection of HF gas in FT-IR absorption spectroscopy (32 scans at 0.5 cm^{-1} resolution) was approximately 10 ppm (approximately 0.001 absorbance units). The absorption techniques give similar limits of detection because the increased signal-to-noise ratio achieved when using phase-sensitive detection with the NIR-TDL ($\nu = 0 - 2$) is offset by the higher absorption coefficient for the fundamental transition measured via FT-IR absorption

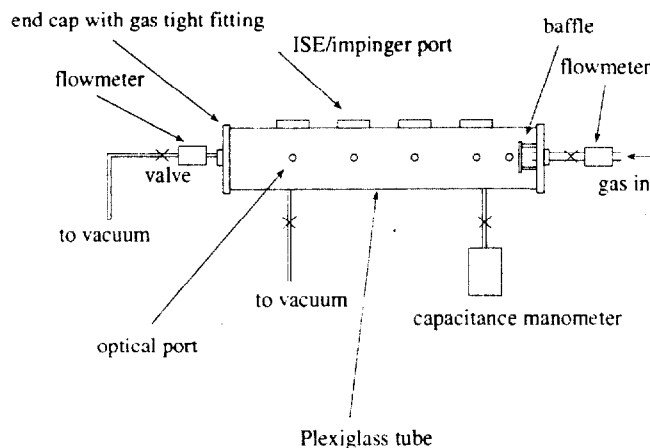


Fig. 3. The flow tube designed to allow simultaneous measurement of HF gas using NIR-TDL absorption spectroscopy, FT-IR spectroscopy, and fluoride-ion selective electrode (ISE). There are five feedthrough ports (one for the ISE, plus four optical ports) per longitudinal position

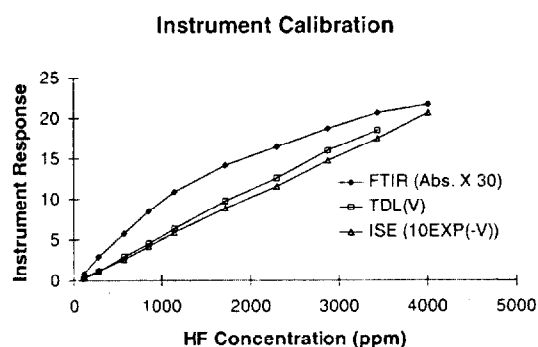


Fig. 4. Results of comparative calibration of FT-IR, NIR-TDL, and fluoride-ion selective electrode for HF gas detection

spectroscopy (the absorption coefficient for HF gas decreases by approximately 20 from the fundamental transition to the first overtone). The non-linearity of the FT-IR absorbance versus concentration data is caused by an interpolation error that occurs because the instrument resolution (0.5 cm^{-1}) is larger than the linewidth being measured. Fitting the entire ro-vibrational envelope of the FT-IR spectrum results in improved linearity. We estimate the error in the spectral measurements to be a few percent, with the error at decreasing HF gas partial pressures approaching the limit of detection (LOD) for each technique. The limit of detection for HF gas in the ISE was approximately 1 ppm. It should be pointed out that the ISE measures the total fluoride-ion concentration, so the technique is unable to distinguish between HF and CF_2O , which is produced in appreciable quantities during chemical suppression of large-scale fires [3].

6 Results and discussion

Measurements of HF gas partial pressures in well-controlled, optically thin environments such as described in the previous section are necessary to check on instrument performance and calibration, but may not reveal difficulties encountered in many laboratory and real-scale tests. In this section we describe measurements of HF gas taken with NIR-TDL ab-

sorption spectroscopy in an atmospheric-pressure opposed-flow propane/air flame suppressed by C_3F_7H (trade name FM-200) and in a 30-KW heptane/air pan fire during extinguishment by a hybrid suppression system [$C_3F_6H_2$ (trade name FE-36) plus particulate] designed to scavenge HF gas.

6.1 Laboratory flame suppression studies

Figure 5 shows a schematic of an opposed flow burner apparatus and the positioning of the fiber-optic GRIN lens assembly and detector used to measure HF gas produced in a propane/air/fluorocarbon flame. By varying the mass flow rate of the fuel and oxidizer for a given flame in the opposed-flow burner, the mole fraction of a given suppressant needed for extinguishment may be varied. The ability to vary the "strength" of a flame in the opposed flow burner ("strength" being inversely proportional to the ratio of diffusion to chemical times, referred to as the Damkohler number) [12] allows flames of different strengths to be investigated and allows for a ranking of Halon alternatives according to their flame suppression efficiency.

Figure 6 shows the results of NIR-TDL measurement of HF gas produced in a propane/air opposed-flow flame (strain rate = 50 cm^{-1}) to which 1% C_3F_7H (trade name FM-200) has been added to the air stream. To generate this data, the fiber-optic GRIN lens assembly and detector were kept fixed in position and the burner assembly was translated vertically. In this figure, raw data (peak-to-trough distance of the $2f$ waveform; see, for example, Fig. 2) are represented by symbols, and data corrected for changes in baseline DC level are shown by a line. The DC output level of the detector was measured by a LeCroy model 9354 oscilloscope, DC coupled (bandwidth 500 MHz). For measurements made in this flame system, the change in DC baseline level as different heights in the flame are probed is caused by density gradients which cause beam steering when the line-of-sight is in the vicinity of the luminous zone of the flame. The data shown are not corrected for temperature (peak temperature is approximately 2000 K) so may not be used as a direct measure of HF gas

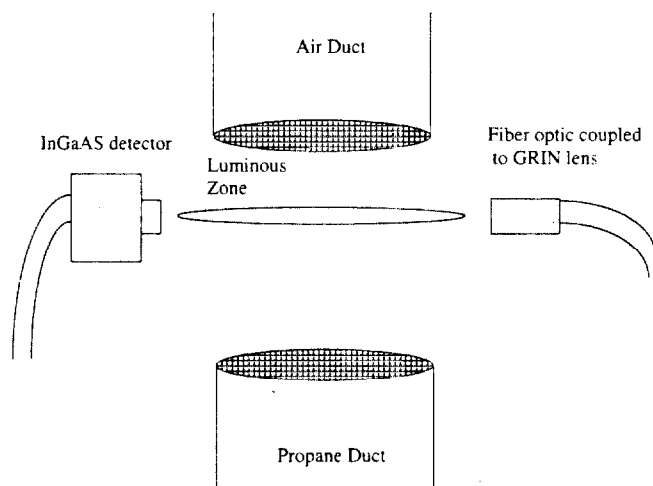


Fig. 5. Schematic of the atmospheric-pressure opposed-flow burner, fiber-optic coupled to GRIN lens for delivery of laser radiation, and InGaAs detector element

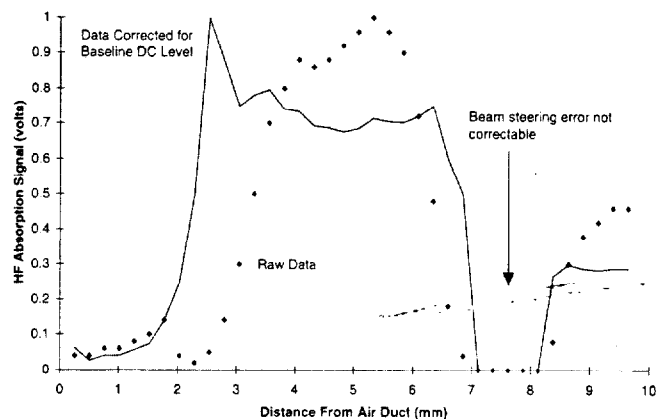


Fig. 6. HF gas absorption versus distance from the oxidizer duct for an atmospheric-pressure-opposed flow propane/air flame to which 1% C_3F_7H has been added to the air stream. The symbols are raw data, the line represents the data corrected for fluctuations in DC baseline signal level

partial pressures. By using $2f$ detection, these beam-steering-induced errors may be compensated for as long as some laser radiation reaches the detector. It should be emphasized that for large decreases in DC signal level caused by beam steering, the large correction increases measurement error. For the experiments reported here, no attempt was made to quantify this source of error. The case where no correction is possible may be seen in the region from 7 to 8 mm from the oxidizer duct. In this region, no laser radiation was incident on the detector.

6.2 Field flame suppression studies

Figure 7 shows results of preliminary NIR-TDL measurement of HF gas in a test designed to measure the effect of particulates designed to scavenge HF. For these tests, a fiber-optic GRIN lens and detector assembly (pathlength = 10 cm) was placed in a 1.5-m^3 cubic enclosure near an air-fed liquid-heptane pan fire (fire size approximately 30 KW). After the

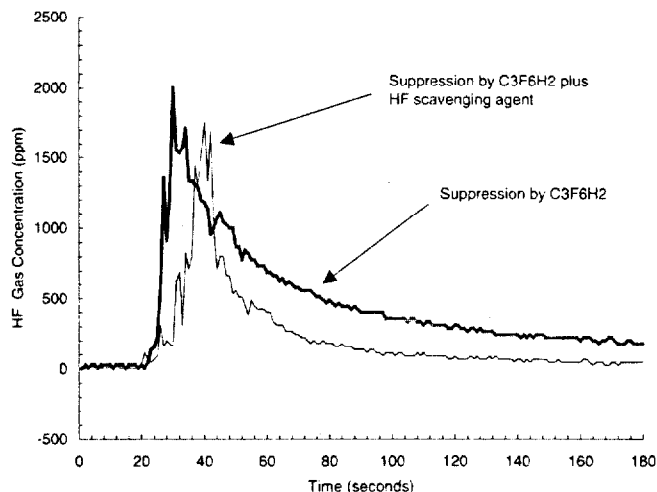


Fig. 7. HF gas concentration versus time for heptane pan fires suppressed by C_3F_8 with and without addition of HF scavenging agent. Note the difference in the rate at which HF gas concentration decreases with and without scavenging agent

fire was allowed to burn uninhibited for 15 s, the enclosure was flooded with 10 vol. % $C_3F_6H_2$ (trade name FE-36), with and without the particulate matter additive. A new data point was measured every 10 ms. During the test, temperatures at the detector photodiode ranged from 300 K to 380 K. No correction was applied to the spectra to account for this temperature change.

Figure 7 shows that the rate at which HF gas concentration decreases after peak concentration is reached is fastest for the fire extinguished by FE-36 to which particles have been added. For this test, the measurement indicates that the particulate matter added to the fluorocarbon-based suppressant (FE-36) successfully reduced the time-weighted average HF concentration. It should be mentioned that there was no check on the calibration of the particle-filled environments, so we do not have an estimate of the variation in error with particle number density. We are currently in the process of evaluating such a calibration system.

7 Conclusion

NIR-TDL laser absorption spectroscopy is an extremely useful tool for measuring HF gas concentrations produced during fire suppression by fluorocarbon-based suppressants. The low cost of fiber optics and detectors allows for real-time in-situ measurement of HF gas in hostile environments. Care must be taken to ensure calibration is maintained during testing because optic surfaces may be damaged during measurement.

Future experiments will involve multiplexing of several lasers to enable multiple species to be measured by using one fiber and one detector. Additionally, recent advances in laser fabrication have made diode lasers at wavelengths near $2\ \mu\text{m}$ commercially available. This advance improves limits of detection for many species by decreasing the quantum number change in absorption, as well as enabling measurement of

species whose highest lying fundamental has up to now been out of reach of commercially available near-infrared laser diodes.

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